Supporting Information

Copper Nanoparticle-Catalyzed Borylation of Alkyl Bromides with Organodiboron Compound

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I. General Information

Chemicals and Reagents All solvents were dried and distilled according to standard methods before use. Solvents utilized in this work were obtained from Sigma-Aldrich (anhydrous \(N,N\)-dimethylformamide) and Samchun Pure Chemicals (hexanes, ethyl acetate, diethyl ether, dichloromethane and acetone).

Copper nanoparticles (25–40 nm) were purchased from SkySpring Nanomaterials, Inc. (2935 Westhollow Dr., Houston, TX 77082, USA). Copper(II) oxide nanoparticle were purchased from Sigma-Aldrich.

\(n\)-Hexane, diethyl ether and ethyl acetate were used without further purification. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, or TCI and were used as received. 6-Bromo-N,N-diethylhexanamide\(^1\) (Table 1, entries 20-21), 2-(6-bromohexyloxy)tetrahydro-2H-pyran and 1-(4-bromobuty1)-1H-indole\(^2\) were prepared according to literature procedures. Bis(pinacolato)diboron were purchased from Sigma-Aldrich. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel plates (60F-254). The TLC plates were visualized by UV-light (254 nm) and treatment with acidic \(p\)-anisaldehyde and KMnO\(_4\) stain followed by gentle heating. Workup procedures were done in air. Flash column chromatography was carried out on Merck 60 silica gel (230 – 400 mesh).

Physical Methods \(^1\)H and \(^{13}\)C NMR spectra were recorded with Agilent 400-MR DD2 (400 MHz and 100 MHz, respectively) spectrometer. \(^1\)H NMR spectra were taken in CDCl\(_3\) and were referenced to residual TMS (7.26 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet). Chemical shifts of the \(^{13}\)C NMR spectra were measured relative to CDCl\(_3\) (77.00 ppm). \(^{11}\)B NMR spectra were recorded with Jeol JNM-LA400 with LFG (128 MHz, respectively) at NICEM. High-Resolution Mass Spectra were obtained at the Korea Basic Science Institute (Daegu, South Korea) on a Jeol JMS 700 high resolution mass spectrometer. GC-MS analyses were performed with a HP-6890 series with a HP-5 capillary column (30 m x 0.25 mm; coating thickness 0.25 \(\mu\)m) and Agilent 5973 Network Mass Selective detector. Analytical condition – initial temperature : 50 °C, raising temperature 10 °C / min, final temperature : 280 °C, He gas, Pressure : 7.56 psi, Total flow : 53.7 mL / min.
**II. General Procedure for the entries reported Table 1 from alkyl bromides**

Reactions were performed in a schlenk tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 5 mg (c.a. 15 mol%) of catalyst (stored in a glove box), 0.5 mmol of alkyl bromide, 2 equiv (0.75 g) of base, 1.5 equiv (0.19g) of bis(pinacolato)diboron and 1 mL of DMF. The mixture was stirred at room temperature for 3 h. The reaction mixture was filtered over a silica gel pad using ethyl acetate and diethyl ether and the filtrate was evaporated under reduced pressure. The concentrated reaction mixture was purified by flash chromatography on silica gel (n-hexane/ethyl acetate) to afford the product.

**Characterization Data for the Isolated Products**

![Structural formula of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane]

4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane: colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.41 – 1.34 (m, 2 H), 1.31 – 1.23 (m, 10 H), 1.23 (s, 12 H), 0.85 (t, $J$ = 6.9 Hz, 3 H), 0.77 – 0.72 (m, 2 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 82.8, 32.4, 31.9, 29.4, 29.2, 24.8, 24.0, 22.7, 14.1, 11.2.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.3.

HRMS (EI) calc. for [C$_{14}$H$_{29}$BO$_2$, M]$^+$ 240.2261, found 240.2257.

![Structural formula of 2-(2-(1,3-dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane]

2-(2-(1,3-dioxan-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.45 (t, $J$ = 5.1 Hz, 1 H), 4.09 – 4.03 (m, 2 H), 3.76 – 3.67 (m, 2 H), 2.10 – 1.97 (m, 1 H), 1.69 (td, $J$ = 7.7, 5.2 Hz, 2 H), 1.32 – 1.26 (m, 1 H), 1.21 (s, 12 H), 0.80 (t, $J$ = 7.7 Hz, 2 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 103.1, 82.8, 82.8, 66.7, 29.4, 25.8, 24.9, 24.7, 5.3.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.0.

HRMS (FAB) calc. for [C$_{12}$H$_{23}$BO$_4$, M-H]$^+$ 241.1611, found 241.1608.

![Structural formula of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane]

4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane: colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.20 (m, 4 H), 7.19 – 7.12 (m, 1 H), 2.78 – 2.72 (m, 2 H), 1.22 (s, 12 H), 1.18 – 1.12 (m, 2 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.3, 128.1, 127.94, 125.44, 83.03, 77.32, 77.00, 76.68, 29.91, 24.76, 12.95.
HRMS (EI) calc. for [C\textsubscript{14}H\textsubscript{21}BO\textsubscript{2}, M]\textsuperscript{+} 232.1635, found 232.1637.

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\textbf{5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl acetate:} colorless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 3.99 (t, \(J = 6.8\) Hz, 2 H), 1.99 (s, 3 H), 1.63 – 1.52 (m, 2 H), 1.44 – 1.35 (m, 2 H), 1.35 – 1.27 (m, 2 H), 1.19 (s, 12 H), 0.76 – 0.70 (m, 2 H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 171.0, 82.7, 64.4, 28.4, 28.2, 24.7, 23.5, 20.9, 11.0.

HRMS (FAB) calc. for [C\textsubscript{13}H\textsubscript{25}BO\textsubscript{4}, M+H]\textsuperscript{+} 257.1924, found 257.1927.

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\textbf{5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-ol:} colorless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 3.60 (t, \(J = 6.5\) Hz, 2 H), 1.63 (s, 1 H), 1.54 (dt, \(J = 13.1, 6.5\) Hz, 2 H), 1.45 – 1.38 (m, 2 H), 1.38 – 1.31 (m, 2 H), 1.22 (s, 12 H), 0.77 (t, \(J = 7.4\) Hz, 2 H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 82.9, 62.8, 32.4, 28.3, 24.8, 23.6, 11.0.

HRMS (FAB) calc. for [C\textsubscript{11}H\textsubscript{23}BO\textsubscript{3}, M+H]\textsuperscript{+} 215.1819, found 215.1820.

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\textbf{6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanenitrile:} colorless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 2.30 (t, \(J = 7.2\) Hz, 2 H), 1.67 – 1.57 (m, 2 H), 1.45 – 1.39 (m, 4 H), 1.21 (s, 12 H), 0.76 (t, \(J = 7.3\) Hz, 2 H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 119.8, 83.0, 31.1, 25.0, 24.7, 23.0, 16.9, 10.7.

HRMS (EI) calc. for [C\textsubscript{12}H\textsubscript{22}BNO\textsubscript{2}, M]\textsuperscript{+} 223.1744, found 223.1741.

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\textbf{4,4,5,5-tetramethyl-2-(2-phenoxyethyl)-1,3,2-dioxaborolane:} colorless liquid.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.30 – 7.21 (m, 2H), 6.91 (t, \(J = 7.6\) Hz, 3 H), 4.10 (t, \(J = 7.8\) Hz, 2 H), 1.37 (t, \(J = 7.8\) Hz, 2 H), 1.26 (s, 12 H).

\textsuperscript{13}C NMR (100MHz, CDCl\textsubscript{3}) \(\delta\) 159.0, 129.2, 120.3, 114.6, 83.3, 64.7, 24.7, 12.6.

HRMS (EI) calc. for [C\textsubscript{12}H\textsubscript{22}BNO\textsubscript{2}, M]\textsuperscript{+} 223.1744, found 223.1741.
**N,N-diethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide:** colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.31 (q, $J = 7.1$ Hz, 2 H), 3.25 (q, $J = 7.1$ Hz, 2 H), 2.25 – 2.20 (m, 2 H), 1.59 (dt, $J = 15.3$, 7.6 Hz, 2 H), 1.44 – 1.34 (m, 2 H), 1.34 – 1.24 (m, 2 H), 1.19 (s, 12 H), 1.11 (t, $J = 7.1$ Hz, 3 H), 1.05 (t, $J = 7.1$ Hz, 3 H), 0.73 (t, $J = 7.6$ Hz, 2 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.2, 82.8, 41.9, 39.9, 33.1, 32.3, 25.3, 24.7, 23.8, 14.3, 13.1, 11.1.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.1.

HRMS (EI) calc. for [C$_{14}$H$_{21}$BO$_3$, M]$^+$ 248.1584, found 248.1582.

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**2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:** colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 – 7.18 (m, 4 H), 7.14 – 7.11 (m, 1 H), 2.30 (s, 2 H), 1.24 (s, 12 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.6, 128.9, 128.2, 124.8, 83.3, 24.7, 19.8.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 32.2.

HRMS (EI) calc. for [C$_{13}$H$_{19}$BO$_2$, M]$^+$ 218.1478, found 218.1481.

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**4,4,5,5-tetramethyl-2-(5-((tetrahydro-2H-pyran-2-yl)oxy)pentyl)-1,3,2-dioxaborolane:** colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.55 – 4.52 (m, 1 H), 3.88 – 3.80 (m, 1 H), 3.68 (dt, $J = 9.6$, 6.9 Hz, 1 H), 3.49 – 3.42 (m, 1 H), 3.34 (dt, $J = 9.6$, 6.7 Hz, 1 H), 1.84 – 1.74 (m, 1 H), 1.71 – 1.63 (m, 1 H), 1.61 – 1.45 (m, 6 H), 1.43 – 1.30 (m, 4 H), 1.20 (s, 12 H), 0.74 (t, $J = 7.6$ Hz, 2 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 98.7, 82.8, 67.5, 62.2, 30.7, 29.5, 29.0, 25.4, 24.7, 23.8, 19.6, 11.1.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.2.

HRMS (EI) calc. for [C$_{16}$H$_{31}$BO$_4$, M-H]$^+$ 297.2237, found 297.2236.

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**1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1H-indole:** pale yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 7.9$ Hz, 1 H), 7.37 (dd, $J = 8.2$, 0.6 Hz, 1 H), 7.25 – 7.19 (m, 1 H),...
7.13 – 7.09 (m, 2 H), 6.50 (dd, \(J = 3.1, 0.7\) Hz, 1 H), 1.88 (ddd, \(J = 15.1, 11.2, 7.6\) Hz, 2 H), 1.50 (dt, \(J = 15.4, 7.7\) Hz, 2 H), 1.25 (s, 12 H), 0.85 (t, \(J = 7.7\) Hz, 2 H).

\(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\) \(\delta\) 135.8, 128.5, 127.7, 121.1, 120.8, 119.0, 109.4, 100.7, 83.0, 46.2, 32.6, 24.8, 21.4, 10.8 .

\(\text{\(^{11}\)B NMR (128 MHz, CDCl}_3\) \(\delta\) 33.2.}

HRMS (EI) calc. for \([\text{C}_{18}\text{H}_{26}\text{BNO}_2, \text{M}]^+\) 299.2057, found 299.2059.

\[\text{2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: colorless liquid.}
\]

\(\text{\(^1H NMR (400 MHz, CDCl}_3\) \(\delta\) 1.70 – 1.50 (m, 5 H), 1.42 – 1.24 (m, 5 H), 1.22 (s, 12 H), 1.01 – 0.90 (m, 1 H).}

\(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\) \(\delta\) 82.7, 27.9, 27.1, 26.7, 24.7, 22.1 .}

\(\text{\(^{11}\)B NMR (128 MHz, CDCl}_3\) \(\delta\) 33.2}

HRMS (EI) calc. for \([\text{C}_{12}\text{H}_{23}\text{BO}_2, \text{M}]^+\) 210.1791, found 210.1792.

\[\text{2-cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: colorless liquid.}
\]

\(\text{\(^1H NMR (400 MHz, CDCl}_3\) \(\delta\) 1.78 – 1.68 (m, 2 H), 1.61 – 1.53 (m, 2 H), 1.52 – 1.38 (m, 4 H), 1.21 (s, 12 H), 1.17 – 1.11 (m, 1 H).}

\(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\) \(\delta\) 82.7, 28.5, 26.8, 24.7, 22.0 .}

\(\text{\(^{11}\)B NMR (128 MHz, CDCl}_3\) \(\delta\) 33.7.}

HRMS (EI) calc. for \([\text{C}_{11}\text{H}_{21}\text{BO}_2, \text{M}]^+\) 196.1635, found 196.1636.

\[\text{4,4,5,5-tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane: colorless liquid.}
\]

\(\text{\(^1H NMR (400 MHz, CDCl}_3\) \(\delta\) 7.26 – 7.18 (m, 4 H), 7.16 – 7.11 (m, 1 H), 2.80 (dd, \(J = 13.6, 7.6\) Hz, 1 H), 2.54 (dd, \(J = 13.6, 8.3\) Hz, 1 H), 1.43 – 1.34 (m, 1 H), 1.18 (s, 12 H), 0.97 (d, \(J = 7.4\) Hz, 3 H).}

\(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\) \(\delta\) 142.2, 128.8, 127.9, 125.5, 82.9, 83.9, 24.6, 18.9, 15.2 .}

\(\text{\(^{11}\)B NMR (128 MHz, CDCl}_3\) \(\delta\) 33.4.}

HRMS (EI) calc. for \([\text{C}_{15}\text{H}_{23}\text{BO}_2, \text{M}]^+\) 246.1791, found 246.1789.

\[\text{tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate: colorless liquid.}
\]
$^1$H NMR (400 MHz, CDCl$_3$) δ 3.80 – 3.67 (m, 2 H), 2.95 – 2.80 (m, 2 H), 1.62 – 1.54 (m, 2 H), 1.48 – 1.40 (m, 2 H), 1.39 (s, 9 H), 1.18 (s, 12 H), 1.09 – 1.01 (m, 1 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.7, 83.0, 78.9, 44.3(broad), 28.4, 26.8, 24.6, 19.7 .

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 32.8.

HRMS (El) calc. for [C$_{16}$H$_{30}$BNO$_4$, M]$^+$ 311.2268, found 311.2271.

![Structure](image)

**2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**: colorless liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.94 – 5.80 (m, 1 H), 5.03 – 4.93 (m, 1 H), 4.90 – 4.83 (m, 1 H), 2.16 (td, $J$ = 7.7, 1.2 Hz, 2 H), 1.23 (s, 12 H), 0.87 (t, $J$ = 7.7 Hz, 2 H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.7, 113.1, 83.0, 28.0, 24.8, 10.4.

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 33.1.

![Structure](image)

**exo-2-(Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.28 – 2.24 (m, 1 H), 2.22 – 2.17 (m, 1 H), 1.58 – 1.45 (m, 3 H), 1.38 – 1.23 (m, 3 H), 1.20 (s, 12 H), 1.18 – 1.10 (m, 2 H), 0.89 – 0.83 (m, 1 H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 82.7, 38.7, 38.1, 36.6, 32.2, 32.1, 29.2, 24.7.

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 33.2

HRMS (El) calc. for [C$_{13}$H$_{23}$BO$_2$, M]$^+$ 222.1791, found 222.1793.

**References**


VI. NMR Spectra of Isolated Products